

1 What is Claimed is:

2 1. A method for removing nitrogen interference in pyro-electrochemical methods of  
3 analysis, the method comprising the steps of:

- 4 a. thermally oxidizing a sample to produce a sample gas;  
5 b. selectively removing a nitrogen-containing interferant from the sample gas;  
6 c. cooling the sample gas; and  
7 d. detecting the substance with an electrochemical detector.

1 2. The method of claim 1, wherein the selective removal is accomplished by using a  
2 scrubber.

1 3. The method of claim 1, wherein the selective removal step comprises selectively  
2 converting the nitrogen-containing interferant into a non-interfering species.

1 4. The method of claim 3, wherein the nitrogen-containing interferant is  $\text{NO}_2$  and further  
2 wherein the  $\text{NO}_2$  is selectively converted to  $\text{NO}$ .

1 5. The method of claim 3, wherein the selective conversion step is accomplished by using a  
2 catalyst.

1 6. The method of claim 5, wherein the catalyst is present in a catalytic converter.

1 7. The method of claim 3, wherein the selective conversion step is accomplished by using a  
2 thermal converter.

1 8. The method of claim 3, further comprising a second selective removal step accomplished  
2 by using a scrubber.

1 9. The method of claim 5, wherein the catalyst is in the form of chips or turnings.

1 10. The method of claim 5, wherein the catalyst is in the form of wire, foil or screen.

1 11. The method of claim 5, wherein the catalyst consists of a series of screens.

- 1 12. The method of claim 5, wherein the catalyst is Group VIB transition metal.
- 1 13. The method of claim 12, wherein the catalyst is molybdenum.
- 1 14. The method of claim 12, wherein the catalyst operates in the range of about 300°C to  
2 about 550°C.
- 1 15. The method of claim 14, wherein the catalyst operates in the range of about 350°C to  
2 about 450°C.
- 1 16. The method of claim 1, wherein the detected substance is a sulfur-containing species.
- 1 17. The method of claim 16, wherein the detected substance is SO<sub>2</sub>.
- 1 18. The method of claim 1, wherein the pressure drop through the selective removal step is  
2 between about 0 to about 10 inches of water.
- 1 19. The method of claim 18, wherein the pressure drop through the selective removal step is  
2 less than 1 inch of water.
- 1 20. The method of claim 1, wherein the selective removal of the nitrogen-containing  
2 interferant is from about 90% to about 100% conversion.
- 1 21. The method of claim 20, wherein the selective removal of the nitrogen-containing  
2 interferant is from about 94% to about 100% conversion.
- 1 22. The method of claim 21, wherein the selective removal of the nitrogen-containing  
2 interferant is from about 96% to about 100% conversion.
- 1 23. The method of claim 1, wherein the sample is cooled to ambient temperature within a  
2 period of about 0 to about 5 seconds.
- 1 24. The method of claim 23, wherein the sample is cooled to ambient temperature within a  
2 period of about 1 second.

- 1 25. The method of claim 3, wherein the thermal oxidation is accomplished using a pyrolysis  
2 furnace, and where the pyrolysis furnace is effective to control the temperature of the  
3 selective conversion step.
- 1 26. The method of claim 1, wherein the flow rate of the sample through the selective removal  
2 step is about 400 to about 800 sccm.
- 1 27. The method of claim 26, wherein the flow rate of the sample through the selective  
2 conversion step is about 650 sccm.
- 1 28. An apparatus for measuring the concentration of a substance in a sample and effective in  
2 removing nitrogen interference in pyro-electrochemical methods comprising:  
3 a. a thermal oxidizer;  
4 b. a removal device for selectively removing the nitrogen-containing interferant  
5 from the sample gas; and  
6 c. a detector, wherein the detector comprises an assembly of one or more  
7 electrochemical cells capable of detecting the substance.
- 1 29. The apparatus of claim 28, wherein the removal device is a scrubber.
- 1 30. The apparatus of claim 28, wherein the removal device selectively converts the  
2 nitrogen-containing interferant into a non-interfering species.
- 1 31. The apparatus of claim 30, wherein the removal device is a thermal converter.
- 1 32. The apparatus of claim 30, wherein the removal device comprises a catalyst.
- 1 33. The apparatus of claim 32, wherein the removal device is a catalytic converter.
- 1 34. The apparatus of claim 28, wherein the removal device comprises a scrubber and a  
2 converter.
- 1 35. The apparatus of claim 32, wherein the catalyst is in the form of chips or turnings.

- 1 36. The apparatus of claim 32, wherein the catalyst is in the form of wire, foil, or screen.
- 1 37. The apparatus of claim 32, wherein the catalyst consists of a series of screens.
- 1 38. The apparatus of claim 32, wherein the catalyst is Group VIB transition metal.
- 1 39. The apparatus of claim 38, wherein the catalyst is molybdenum.
- 1 40. The apparatus of claim 38, wherein the catalyst is operative in the range of about 300°C  
2 to about 550°C.
- 1 41. The apparatus of claim 40, wherein the catalyst is operative in the range of about 350°C  
2 to about 450°C.
- 1 42. The apparatus of claim 29, wherein the thermal oxidizer additionally comprises a  
2 temperature control device, the temperature control device being effective for controlling  
3 the temperature of the removal device.
- 1 43. The apparatus of claim 29, wherein the removal device additionally comprises a  
2 temperature control device.
- 1 44. The apparatus of claim 42, wherein the removal device additionally comprises a separate  
2 temperature control device.
- 1 45. The apparatus of claim 29, wherein the removal device is composed of a material that is  
2 inert to the sample gas.
- 1 46. The apparatus of claim 45, wherein the material is capable of withstanding temperatures  
2 of up to about 550°C.
- 1 47. The apparatus of claim 46, wherein the material is stainless steel or quartz.
- 1 48. The apparatus of claim 29, wherein the removal device comprises a housing, a first end  
2 cap and a second end cap

- 1 49. The apparatus of claim 35, additionally comprising a catalyst retainer to hold the catalyst  
2 in place.
- 1 50. The apparatus of claim 49, wherein the catalyst retainer is stainless steel screen,  
2 molybdenum screen, quartz wool or a permeable quartz plug.
- 1 51. The apparatus of claim 48, wherein the housing additionally comprises an input and an  
2 output tube.
- 1 52. The apparatus of claim 51, wherein the input and output tubes are composed of stainless  
2 steel.
- 1 53. The apparatus of claim 38, wherein the converter operates at a temperature between about  
2 300°C to about 550°C.
- 1 54. The apparatus of claim 53, wherein the converter operates at a temperature between about  
2 350°C to about 450°C.
- 1 55. The apparatus of claim 29, wherein the thermal oxidizer is insulated.
- 1 56. The apparatus of claim 29, wherein the removal device is insulated.
- 1 57. The apparatus of claim 29, wherein the removal device is located in a temperature  
2 controlled enclosure separate from that of the thermal oxidizer.
- 1 58. A method for removing nitrogen interference in pyro-electrochemical methods of  
2 analysis, said method comprising the steps of:
- 3 a. thermally oxidizing a sample in a pyrolysis furnace to produce a sample gas;
- 4 b. selectively converting NO<sub>2</sub> in the thermally oxidized sample gas to NO, wherein  
5 the selective conversion step is accomplished using a catalytic converter having a  
6 molybdenum catalyst, further wherein the catalyst operates in the range of about  
7 300°C to about 550°C, and wherein the flow rate through the catalytic converter is

8 about 400 to about 800 sccm, and further wherein the pressure drop through the  
9 catalytic converter is less than about 1 inch of water;

10 c. cooling the sample gas, wherein the sample gas is cooled to ambient temperature  
11 within about one second after the selective conversion step; and

12 d. detecting the substance using an electrochemical detector.

1 59. An apparatus for measuring the concentration of a substance in a sample and effective in  
2 removing nitrogen interference in pyro-electrochemical methods comprising:

3 a. a thermal oxidizer;

4 b. a converter, wherein said converter is effective for selectively converting the NO<sub>2</sub>  
5 in a sample to NO, and wherein the converter is a catalytic converter having a  
6 molybdenum catalyst, and wherein said converter further comprises a housing and  
7 an input and an output tube, and wherein said converter is composed of a material  
8 that is inert to the sample gas; and

9 c. a detector, wherein the detector comprises an assembly of one or more  
10 electrochemical cells capable of detecting the substance.

1 60. The apparatus of claim 59, wherein the converter operates at a temperature between about  
2 300°C to about 550°

1 61. The apparatus of claim 60, wherein the thermal oxidizer additionally comprises a  
2 temperature control device, the temperature control device being effective for controlling  
3 the temperature of the converter.

1 62. The apparatus of claim 60, wherein the converter additionally comprises a temperature  
2 control device.

1 63. The apparatus of claim 60, wherein the thermal oxidizer is insulated, and further wherein  
2 the converter is insulated.

1 64. The apparatus of claim 60, wherein the converter is located in a temperature controlled  
2 enclosure separate from that of the thermal oxidizer.

1 65. An on-stream analyzer for measuring the concentration of a substance in a fluid sample,  
2 said analyzer comprising:

3 a. a sample injector for injecting the sample at a preset and controlled rate, the  
4 sample injector further comprising a pressure regulator coupled to a flow  
5 restrictor to control the rate of sample flow;

6 b. a thermal oxidizer comprising a tube furnace and a pyrolysis tube, connected to  
7 the sample injector;

8 c. a converter, wherein said converter is effective for selectively converting the  $\text{NO}_2$   
9 in a sample to  $\text{NO}$ , and wherein the converter is a catalytic converter having a  
10 molybdenum catalyst, and wherein said converter further comprises a housing and  
11 an input and an output tube, and wherein said converter is composed of a material  
12 that is inert to the sample gas;

13 d. a sample conditioner, connected to and located downstream from the thermal  
14 oxidizer, to control the conditions of a resulting gas mixture; and

15 e. a detector, connected to the sample conditioner, to measure the concentration of  
16 an oxidized substance contained within the gas mixture.

1 66. An on-stream analyzer for detecting a substance in a fluid sample, said analyzer  
2 comprising:

3 a. a fluid sample injector;

- 4 b. a thermal oxidizer, connected to the sample injector, wherein the sample is  
5 injected into the thermal oxidizer and a carrier gas and a pyrolysis gas are  
6 introduced to the sample under oxidation conditions;
- 7 c. a converter, wherein said converter is effective for selectively converting the  $\text{NO}_2$   
8 in a sample to  $\text{NO}$ , and wherein the converter is a catalytic converter having a  
9 molybdenum catalyst, and wherein said converter further comprises a housing and  
10 an input and an output tube, and wherein said converter is composed of a material  
11 that is inert to the sample gas;
- 12 d. a sample conditioner, connected to the thermal oxidizer, to control the conditions  
13 of a resulting mixture, wherein the conditioner further comprises a dryer for  
14 removing water vapor, wherein the dryer further comprises two concentric tubes,  
15 an inner tube composed of a membrane for transferring water vapor and an outer  
16 tube composed of an inert material, wherein the dryer is configured to operate so  
17 that a dry purge gas is directed through the inner tube and the sample gas is  
18 directed through the annular space between the inner and outer tube, and further  
19 wherein the inner tube is connected to a flow restrictor having an orifice to  
20 maintain positive pressure; and
- 21 e. one or more electrochemical cells, connected to the sample conditioner, to  
22 measure the concentration of a substance contained within the sample.

1 67. A method for detecting a substance in a sample comprising the steps of:

- 2 a. providing a sample in vapor state;
- 3 b. controlling the flow rate of the sample using a pressure regulator coupled to a  
4 fixed flow restrictor;

- 5 c. thermally oxidizing the sample;
- 6 d. selectively converting  $\text{NO}_2$  in the sample to  $\text{NO}$ , wherein the selective conversion
- 7 step is accomplished using a catalytic converter having a molybdenum catalyst,
- 8 from about  $300^\circ\text{C}$  to about  $550^\circ\text{C}$ , and wherein the flow rate through the catalytic
- 9 converter is about 400 to about 800 sccm, and further wherein the pressure drop
- 10 through the catalytic converter is less than about 1 inch of water;
- 11 e. cooling the sample, wherein the sample is cooled to ambient temperature within
- 12 about one second after the selective conversion; and
- 13 f. detecting a substance within the sample.

1 68. A method for detecting a substance in a sample comprising the steps of:

- 2 a. providing a sample in vapor state;
- 3 b. thermally oxidizing the sample;
- 4 c. conditioning the sample to control the temperature and relative humidity of the
- 5 sample, wherein the temperature is regulated with a heat trace element comprising
- 6 self-limiting electrical heating wires and wherein the relative humidity is
- 7 controlled by a dryer comprising two concentric tubes, an inner tube composed of
- 8 a ion-exchange membrane having sulfonic acid groups and an outer tube
- 9 composed of a fluoropolymer resin or stainless steel, wherein a dry purge gas is
- 10 directed through the inner tube and the sample gas is directed through the annular
- 11 space between the inner and outer tube, and further wherein the inner tube is
- 12 connected to a flow restrictor having an orifice to maintain positive pressure;
- 13 d. selectively converting  $\text{NO}_2$  in the sample to  $\text{NO}$ , wherein the selective conversion
- 14 step is accomplished using a catalytic converter having a molybdenum catalyst,

- 15 from about 300°C to about 550°C, and wherein the flow rate through the catalytic  
16 converter is about 400 to about 800 sccm, and further wherein the pressure drop  
17 through the catalytic converter is less than about 1 inch of water;
- 18 e. cooling the sample, wherein the sample is cooled to ambient temperature within  
19 about one second after the selective conversion; and
- 20 f. detecting a substance within the sample.